



Short communication

Importance of open pore structures with mechanical integrity in designing the cathode electrode for lithium–sulfur batteries



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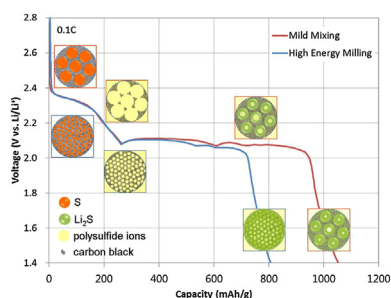
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HIGHLIGHTS

- The Li/S cells can be improved by optimizing the electrode pore structure.
- The capacity of 1000 mAh g⁻¹ at 0.1 C was obtained.
- The stable capacity retention was of >700 mAh g⁻¹ after 200 cycles.
- At 0.5 C, it can be achieved with relatively high sulfur content of 68%.

GRAPHICAL ABSTRACT



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ABSTRACT

The robustness of conductive networks and the accessibility of electrolyte into the network are important factors in designing the cathode electrode for lithium/sulfur (Li/S) batteries containing liquid electrolytes that involve liquid phase electrochemical reactions. We show that the performance of Li/S cells can be significantly improved by simply optimizing the electrode processing conditions to have open pore structures and mechanical integrity of the electrode architecture. It is demonstrated that the capacity of 1000 mAh g⁻¹ at 0.1 C and the stable capacity retention of >700 mAh g⁻¹ after 200 cycles at 0.5 C can be achieved with relatively high sulfur content of 68%. 417 Wh kg⁻¹ in specific energy and 623 Wh l⁻¹ in energy density are achievable with this new technology.

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1. Introduction

With increasing demand for electric transportations that have competitive performance and affordable price, Li/S battery has attracted major attention as a battery system that can overcome the limitation of current lithium-ion technology [1,2]. The expectation

for Li/S battery is rationalized by the high theoretical capacity of sulfur (1672 mAh g⁻¹), which outperforms any known solid cathode material, its natural abundance and environmental benefit [3].

Despite these attractive aspects, there are a number of technical challenges that have been hindering the commercialization of Li/S batteries for decades [4–6]. Firstly, sulfur and its insoluble reaction products (Li₂S₂/Li₂S) are highly resistive in both electron and ion conduction, which limits the reversibility of the sulfur reaction (poor cycle life) and reduces the benefit of energy density because of the need for excessive amount of conductive additives (usually

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carbon). Secondly, the reaction intermediate, polysulfide ions (S_x^{2-} , $8 \leq x \leq 3$) are highly soluble in the liquid electrolytes causing a series of technical issues like low round-trip efficiency, severe self-discharge and parasitic reactions on lithium metal [7].

On the other hand, the high solubility of polysulfide plays a positive role as it allows better utilization of the highly insulating active material by greatly facilitating the contact between the active material and conductive matrix [4]. Without dissolution of polysulfide, only the portion of active material in intimate contact with carbon will be able to participate in the electrochemical reaction. In this regards, the solubility of polysulfide is an important requirement in the liquid electrolyte system [8,9].

Because the initial electrode morphology is not maintained when the soluble polysulfide ions are formed in the first discharge, the traditional approaches to make homogeneous electrode composition are not effective in manufacturing sulfur cathode electrodes. Even the stand-alone conductive carbon layers function effectively as cathode electrodes as long as they are used with the appropriate sulfur sources [10–13]. However, this approach does not address the challenge of lower volumetric energy density due to the presence of low density inactive layers in the cell. To take advantage of the high energy density of sulfur, improvements to Li/S batteries should consider the integrated design of electrodes. In this study, we show that the cell performance is strongly dependent on the electrode process conditions, and investigate the controlling factors influencing the correlation between performance and electrode structure.

2. Experimental

2.1. Powder treatment

Sulfur (Acros, >99%, refined), poly(ethylene oxide) (PEO, Polyscience, MW. 5,000,000) and poly(vinyl pyrrolidone) (PVP, DKS, MW.10,000) were dried under vacuum at 60 °C for 24 h before use. Ketjen Black (EC-600JD) was dried under vacuum at 120 °C for 24 h.

To make the sulfur–carbon composite, a dry mixture of sulfur and Ketjen Black (75:25 by weight) were placed in a stainless steel container filled with Ar gas and blended in a high energy mill (8000M Mixer/Mill, SPEX SamplePrep LLC) for 5–60 min. Stainless steel balls with 2 different diameters (2.5 mm + 4 mm by 1:1 ratio) were used to fill ~30% volume of the container. The operation was interrupted every 10 min to prevent overheating.

2.2. Electrode preparation and cell assembly

The binder solution of PEO (10 wt% in the mixed solvent of acetonitrile + toluene, 8:2 volume ratio) and PVP (10 wt% in absolute ethanol) was added to the as-prepared sulfur–carbon mixture with a ratio of 68:23:8:1 (sulfur:carbon black:PEO:PVP) after drying. Additional solvent (acetonitrile + toluene, 8:2 volume ratio) was added to the slurry to reach a viscosity of ~10,000 cP. Two different mixing conditions were employed to prepare the slurry. For mild mixing, a planetary centrifugal mixer (Thinky Mixer ARE-250) was used for 20 min. For aggressive mixing, a high energy mill (8000M Mixer/Mill, SPEX SamplePrep LLC) was used for 20 min. The slurry was coated on carbon-coated aluminum foil (15 μm) to a loading of 1–2 mg cm^{-2} and carefully dried at 55 °C under mild vacuum.

CR2032 coin cells were assembled in a He-filled glove box using Celgard 3501 as separator and lithium foil (Hoshen, 200 μm) as anode. 0.12 ml of 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in a mixture of ethylene glycol–dimethyl ether (DME) and 1,3-dioxolane (DOX) (1:1 by volume ratio) was injected into the cell. No electrolyte additive was used.

2.3. Electrochemical test and characterization

Electrochemical tests were performed using a VMP cycler (Bio-Logic SAS) at 25 °C. To test the C-rate performance, constant current of 0.1–5 C (1 C = 1672 mA g^{-1}) was applied for both charge and discharge in the voltage range between 1.4 V and 2.8 V vs. Li/Li⁺. Electrochemical impedance spectra were monitored in the frequency range from 200 kHz to 50 mHz with amplitude of 5 mV. Cycle life was tested at 0.5 C constant current in the voltage range between 1.4 V and 2.8 V vs. Li/Li⁺. Before the electrochemical tests, the cells were held at open circuit voltage for 12 h. Scanning electron microscopy (SEM) images were obtained using a field emission scanning electron microscope (Hitachi model S-4700).

3. Results and discussion

As the sulfur particles are easily deformed by both stress and heat, the original morphology of sulfur continuously changes during the electrode preparation process that includes mixing, coating, calendaring and drying. In this study, two different mixing methods were employed to compare the change of morphology and its effects on the electrochemical performance. The first mixing method was done under the relatively mild condition using a planetary centrifugal mixer to preserve the original morphology of pristine materials. In this method, only wet mixing was performed for 20 min without additional treatment of powder. The second mixing method was carried out under more aggressive conditions using a high energy ball mill both in dry power and wet slurry to break down the agglomerates and enhance the sulfur-to-carbon contact. The dry milling was done for 5–60 min followed by wet milling for 20 min.

Fig. 1 shows the morphology of pristine sulfur, which is composed of loose agglomerates of 5–20 micron primary particles, and the sulfur–carbon composite made by dry ball-milling for 30 min. It appears that the sulfur particles are broken and partially melt during the milling process to form the sulfur–carbon composite where the contact area between carbon and sulfur is greatly enhanced. The red arrows in Fig. 1(d) indicate the domain of sulfur spread on the surface of sulfur–carbon composite.

The pores in the carbon particles are partially covered by sulfur in the sulfur–carbon composites, which leads to lower surface area compared with that of the constituent pristine materials. This is reflected in the reduced amount of solvent that is required to make the slurry. The blue line in Fig. 2 shows the content of non-volatile components (sulfur, carbon, binder) in the slurry that is required to reach a viscosity of ~10,000 cP. It appears that the amount of solvent is gradually reduced with milling time and the non-volatile content increases from 14% to 20%. The red line in Fig. 2 shows that the electrodes obtained at longer milling time have a lower porosity. The porosity was calculated by the difference between the specific volume of the electrodes and the true volume of the individual components.

The initial discharge and charge profiles measured with different electrodes are illustrated in Fig. 3. The initial discharge capacity is about 1100 mAh g^{-1} at 0.1 C, irrespective of the electrode preparation conditions. The typical 2-step voltage plateaus corresponding to reduction from solid sulfur (S_8) to soluble polysulfide (Li_2S_x , $x = 8-3$) at the 2.3 V region and the following reduction to insoluble lithium sulfides (Li_2S_2 or Li_2S) at the 2.1 V region are clearly evident. During the rest period (12 h) before starting discharge, the open circuit voltages (2.8–3 V) decrease due to self-discharge from partial solubility of sulfur in the liquid electrolyte. The results in the figure show that self-discharge is accelerated with increasing milling time, probably due to the enhanced exposure of sulfur to the electrolyte when it is in dispersed domains.

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